Development of catalytic microreactors by plasma processes: application to wastewater treatment
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General conclusion and outlooks

The objective of the work presented in the present thesis was to elaborate a catalytic microreactor by plasma processes in order to develop an innovative analytical tool providing unique information on reaction kinetics of catalysed reactions. In the present thesis, synergetic effects between ozone and different catalysts for the oxidation of organic pollutants in water were studied.

In the first chapter, information on the commonly used microfluidic materials as well as catalysts used in heterogeneous catalytic ozonation and ozone refractory pollutants were retrieved from the literature in order to implement a catalytic microreactor using low pressure plasma processes. Polymer-based materials such as PDMS, NOA, THV and COC were identified as suitable microfluidic materials that could possibly withstand low pressure plasma processes. Regarding the nature of the catalysts, iron oxide and cobalt oxide were chosen to be deposited in a low pressure plasma process. Pyruvic acid was chosen as a refractory probe pollutant in order to assess the efficiency of the different catalysts in catalytic ozonation.

Chapter 2 covered the preparation of the thin films. The low pressure plasma processes techniques used for the deposition of the support layer as well as for the catalyst and its activation were described. After a brief theoretical introduction, analytical techniques for the surface characterizations or for the analyses of the collected liquid samples employed in the present work were described.

In Chapter 3, a screening among the polymer-based microfluidic materials identified in the previous chapters was performed by depositing a primer silica-like thin film, acting as a support layer between the catalyst and the polymer substrate, using two different plasma processes, i.e., PECVD and sputtering. Assessed by WCA measurements in air and water storage, aging results showed that the silica-like layer successfully rendered COC, NOA, PDMS and THV hydrophilic for several weeks. However, air aging revealed the instability of the
silica layer on PDMS surfaces due to the well-known hydrophobic recovery of this material. In opposition, the silica-like coated COC appeared to be the most promising for microfluidic applications because of its high stability in terms of hydrophilicity in air and water storage and rapid prototyping compared to THV and NOA. As a consequence, COC was chosen as the starting material for the elaboration of the catalytic microreactor.

Although the aging study showed good results in terms of long-lasting hydrophilicity for the different polymer-based substrates, the different mechanisms involved in the plasma chemistry remains to be studied through the use of in-situ characterization techniques such as Optical Emission Spectroscopy (OES) or Mass Spectroscopy.

As shown in Chapter 4, a MO-PECVD plasma process was used to deposit and activate iron and oxide-based catalysts at low temperatures. Characterization results demonstrated the importance of the plasma post-treatment step, as the latter successfully induced a phase transition change and a structural refinement of the surface of the initial deposited layer for both catalysts. Efficiency of both catalysts was assessed performing catalytic ozonation with pyruvic acid as a refractory probe compound.

In the case of iron oxide layer, HPLC measurements demonstrated the inactivity of the latter, even for the plasma post-treated sample, indicating that the conditions used for the plasma post-treatment were not fully optimized for the iron oxide layer to successfully achieve an adequate crystallization.

In comparison, the decomposition rate of an organic pollutant with ozone was increased in the presence of a cobalt oxide layer. With the plasma deposited cobalt oxide layer, 20% of additional degradation was found whereas the effect
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was doubled (40%) when the layer was post-treated by argon plasma, indicating a synergistic effect between the surface morphology of the coating and PA.

Moreover, the use of plasma processes for the deposition catalyst offers interesting perspectives in the depollution field as it minimizes the potential nanotoxicity of the surface and suggests a long-term viability of the coating as demonstrated with FAAS measurements.

A decrease of the catalytic activity for the post-treated cobalt oxide layer was found indicating a possible coverage of the active sites by intermediate products generated during catalytic ozonation. Nevertheless, it was shown that the catalyst could be regenerated by flushing ozone dissolved in Milli-Q water, indicating that this phenomenon is reversible. Therefore, experiments with a higher ozone concentration are suggested for a better understanding of the catalytic effect on the product selectivity.

In Chapter 5, a numerical study dealing with the reactions taking place on the surface of the post-treated cobalt oxide layer during catalytic ozonation was carried out using the Comsol Multiphysics software. It was shown that the model used to describe the degradation of pyruvic acid in a catalytic microreactor only partially fitted the experimental data.

This could be due to the lack of information concerning the different adsorption and desorption reactions rate constants of the intermediate species generated during the catalytic ozonation step. Indeed, catalytic reactions involve numerous steps which are adsorption, reaction and desorption. Therefore, it is suggested to refine the CFD model developed during this work in order to establish the details of the reaction network between the adsorbed species and gas phase reactions.

At the end of this work, it should be recognized that the complexity of the reaction mechanisms in catalytic microreactors does not allow a simplified analysis. Fundamental advances on numerical models will be required before complete models are successful in modelling the chemical phenomena related to
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interfaces and for instance, providing access to the information on activation energies for various catalyst/reagent couple.

However, this can be achieved through the use of the Coherent Anti-Stokes Raman Spectroscopy technique (CARS technique) as an online analytical tool. Results obtained by the CARS technique would lead to a model that could be used as a tool to predict the relevance and the direction of future improvement strategies regarding catalyzed chemical reactions.